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Geochronology of metamorphic rocks

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ABSTRACT. — Metamorphic minerals are formed at moderate to high depth in the Earth's interior. Those that have been subsequently exhumed to the Earth's surface are those that survived metastably outside their stability fields. The majority of studied metamorphic rocks did not survive unscathed, and contains diachronic mineral assemblages that record a plurality of P-T-A-X conditions along the exhumation path, rather than a single P-T-A-X point that includes all minerals in that rock. Such mixed assemblages are in mutual disequilibrium. Dating a metamorphic event therefore requires great interpretive caution. While an apparent age always results from mathematical equations, translating a number into a geological interpretation can be ambiguous and requires establishing a context among different isotope systems, and even more importantly, between the isotope record and mineralogy, microtextures, and microchemistry. Electron microscopy reveals that many minerals consist of mixtures at the sub-μm scale, as they are intergrown with their retrogression products, and/or contain unequilibrated relics (e.g. zircons, monazites, amphiboles, micas). Lack of chemical homogeneity means that diffusivity under anhydrous conditions is extremely low. Modern, direct determinations of dry diffusion in minerals yield rates that are orders of magnitude slower than what was thought twenty years ago. If recrystallization is incomplete, petrographic relics ensure isotopic inheritance. By contrast, water accelerates recrystallization and so enhances element and isotope reequilibration, both in experiments and in natural systems. Availability of water, not temperature, is the principal factor controlling isotope transport. The isotope record of a mineral is thus a geohygrometer and can be used, but only in connection with petrological constraints, to reconstruct a rock's petrogenetic path.

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RIASSUNTO. — I minerali metamorfici si formano a profondità medie ed alte nell'interno della Terra. Quelli esumati alla superficie sono quelli sopravvissuti metastabilmente al di fuori del loro campo di stabilità. Per la maggior parte, le rocce metamorfiche non sono sopravvissute intatte, ma contengono paragenesi formate diacronicamente che registrano una moltitudine di condizioni P-T-A-X lungo il percorso di esumazione, e non un singolo punto P-T-A-X definito da tutti i minerali di quella roccia. Tali paragenesi miste sono in reciproco disequilibrio. Perciò, datare un evento metamorfico richiede grande cautela nell'interpretazione. Sebbene le equazioni forniscano comunque un risultato numerico, la traduzione di un numero in un'interpretazione geologica può essere ambigua; richiede il saper contestualizzare i vari sistemi isotopici tra loro e, cosa ancora più importante, legarli con mineralogia, microtessiture, e

microchimica. La microscopia elettronica mostra che molti minerali consistono di misture a scala (sub-)micrometrica, nel senso che un minerale può contenere intercrescite dei propri prodotti di alterazione, e/o relitti non equilibrati: tra gli esempi citiamo zirconi, monaziti, anfiboli, e miche. La mancanza di omogeneità chimica significa che la diffusività in condizioni anidre è estremamente bassa. Le determinazioni dirette della diffusività con metodi moderni forniscono velocità di diffusione che sono vari ordini di grandezza inferiori di quanto si pensasse vent'anni fa. Se la ricristallizzazione non è completa, il permanere di relitti petrografici garantisce il permanere di isotopi ereditati. Al contrario, la presenza di acqua accelera la ricristallizzazione e quindi il riequilibrio di elementi ed isotopi, sia negli esperimenti sia nei sistemi naturali. È un dato di fatto che è la presenza dell'acqua, e non la temperatura, a controllare principalmente il trasporto degli isotopi. Bisogna quindi considerare i sistemi isotopici di un minerale come dei geoigrometri che possono essere usati, ma solo in combinazione con i vincoli petrologici, per ricostruire la storia petrogenetica di una roccia.

KEY WORDS: *Geochronology, isotopes, petrology, microchemistry, disequilibrium microtextures*

INTRODUCTION

The age equation for every radioactive decay system requires the accurate knowledge of F_0, the concentration of the daughter isotope that the mineral had at the time when the radiogenic isotope started accumulating. In general, correctly estimating F_0 requires an indirect argument (e.g. Faure, 1974, Chapter 6). Consider a well-stirred magma, which has stayed totally molten for a sufficiently long time to have achieved complete chemical and isotopic equilibrium. When the magma crystallizes, all its minerals have the same isotopic ratio. From such an equilibrium mineral assemblage, an age is then calculated using the isochron diagram, in which isochronous samples define a straight line. The most general mathematical formulation of isochrons is given by Provost (1990).

The requirement of complete isotopic homogenization is less obvious than the pioneers had imagined over 40 years ago. In anatectic magmatic rocks, isotopic disequilibrium has been documented (Ferrara *et al.*, 1989; Christensen *et al.*, 1995). In partial melting of the crustal protolith, restites can survive, and this is observed to prevent isotopic equilibration. It is essential to ascertain whether the microtextures of magmatic rocks only reflect growth from a melt, in which case isotopic equilibration is expected, or if petrographic relics have preserved chemical disequilibrium, causing isotopic inheritance. In this latter case, the whole-rock system (i.e. the sum of all rock-forming and accessory minerals) does not represent the magma from which the minerals crystallized and must not be regressed together with them to obtain an isochron because the calculated age would be incorrect. A special cause of concern is the fact that several of the radioactive parents used by geochronologists are high field strength (HFS) elements and have the tendency to form, or occur in, accessory minerals in which bonds are extremely strong, considerably more so than those of the more abundant minerals such as pyroxenes and feldspars. HFS accessory minerals are very resistant and thence very likely to survive partial melting events.

The analytical improvements over the last 40 years allow us to recognize small but significant deviations from ideality. Therefore, reliable isochrons are overdetermined ones, i.e. those formed by three or more independent points; by allowing a statistical examination of deviations, it is possible to test the isochrons for internal consistency. If data points lie off the regression line by more than their analytical uncertainty, presumably they record a significant geological process which differs from that defined by the other data points. It is an obligation for geochronologists to try and understand the cause of such scatter.

The possibility to detect systematic departures from ideality thanks to improved instruments and lower blanks raises the philosophical question of the difference between precision and accuracy of an analysis. Precision only mirrors random errors, i.e. expresses the likelihood that a duplicate

analysis of the same material will reproduce the obtained value within the analytical uncertainty; accuracy is only affected by systematic errors, i.e. reflects whether a calculated value is right or wrong. Accuracy is thus an undecidable property in the mathematical sense: it cannot be ascertained in the framework of the edifice from which it was derived and its validation requires criteria external to that edifice.

Isochroneity and homogeneity

In the case of metamorphic rocks, the task of finding minerals that fulfill the prerequisites for dating (complete, instantaneous isotopic equilibration of all minerals, homogeneity (absence of inclusions and zonations), lack of retrogressive transformations) is more difficult than in magmatic rocks. Ideally, if the whole rock completely recrystallized during a metamorphic event, dating is as straightforward as for a magmatic rock, since the requirement of isotopic homogeneity is met and an isochron calculation is legitimate. In practice, survival of relics is vastly more frequent than in magmatic rocks, and the whole-rock system is seldom in isotopic equilibrium with any of the minerals it contains. Only if one limits the analysis to inclusion-free parageneses defining metamorphic conditions is it possible to determine an isochron with an accurate age information.

Countless observations document that not all minerals, and/or dating methods, give the same age on one and the same rock. Several explanations for this fact have been proposed. Among the first ones was Jäger's hypothesis, which became very popular on account of its simplicity. Jäger (1973) argued that minerals do not retain radiogenic daughters at high temperature; only if the ambient temperature drops below a certain critical value, termed «blocking temperature» by Jäger, the mineral will quantitatively retain all of the radiogenic daughter isotopes. Jäger based this interpretation on the then available data from the Central Alps, and on the assumption of a single, pan-Alpine metamorphic peak at 38 Ma. Jäger's approach apparently accounted for most of the data it was derived from, and still coarsely accounts for small subsets of data on small areas; however, when partial reconstructions are merged, internal inconsistencies become visible. It cannot correctly predict regional age patterns nor the discrepancies with the large number of mineral chronometers that came into widespread usage after 1970, as discussed in the review by Villa (1998).

When a model attempts to reproduce a set of observations, two questions must be asked: does this model explain the facts? Are there other models that also explain them? It is possible that for a given data set and a given model both answers be yes. In this case, additional data are needed. In the case of the closure of isotopic systems, three classes of additional data, unknown in the 1970s, need to be taken into account: high resolution electron microscopy, modern metamorphic petrology, and diffusion experiments.

The influence of electron microscopy on our perception of minerals cannot be overestimated. Firstly, it documents that «minerals» as they were considered a century ago are no longer so well defined at the 1-10 nm scale and that mixtures and intergrowths are the rule, especially in metamorphic minerals (Hess *et al.*, 1987; Allen, 1992; Veblen, 1992; Belluso *et al.*, 2000). Secondly, it illustrates the frequent presence of sub-μm inclusions. While inclusions *per se* are no indictment of isotopic dating techniques, it is necessary to keep in mind that most radioactive parent nuclides are trace elements. As accessory minerals such as zircon and monazite are especially enriched in rare earth elements (REE), U, and Th, it is intuitive that one sub-μm inclusion of such an accessory phase can dominate the radioactive budget of a «mineral». In turn, it is often impossible to ascertain on textural grounds whether such micro/nanoinclusions are part of an equilibrium paragenesis or are relics of some earlier

metamorphic event, such as the nm-sized inclusions documented by Seydoux-Guillaume *et al.* (2003). Even major minerals, when viewed using back-scattered electron imaging (BSE) or analysed by electron microprobe, frequently show the coexistence of several generations (Di Vincenzo *et al.*, 2001, 2004). Isotopic dating of mixtures requires unravelling the individual ages of the different phases.

Modern metamorphic petrology has come a long way since the thermal-only concept of isograd was introduced. The role of aqueous fluids is now accepted (Cesare *et al.*, 2001), even in such apparently «dry» facies such as eclogites (Philippot and Rumble, 2000). The new understanding can be very crudely summarized as «no metamorphic peak recrystallization without water circulation». As any recrystallizing mineral will re-incorporate trace elements according to their partition coefficients, for most daughter-parent systems and for most minerals a total metamorphic recrystallization entails total expulsion of daughters and resetting of the isotopic age. Villa (1998) conjectured that the reverse is true as well: the preservation of petrographic relics ensures isotopic inheritance. This is motivated by the atomistic nature of diffusion. Regardless of the initial crystallographic site of the daughter isotope, what is by far energetically most costly are the random jumps of the diffusing atom from unit cell to the next, about 10^6 times until the crystal rim is reached. No jump can occur unless the structure is distorted, i.e. structure-forming cations move.

The mobility of structure-forming cations is accelerated by water. Petrology thus provides support to the argument that isotopic exchange is greatly enhanced by the presence of an aqueous fluid. This implies a vague dependence of isotopic exchange on temperature, especially for minerals which are affected by greenschist facies metamorphism, in so far as at higher T there is a higher availability of dehydration water. However, this temperature dependence is not quantitative and should not be used to solve for an unknown T. Since addition of water promotes dissolution/reprecipitation at rates that are much faster than those of anhydrous cation transport, it is clear that there is a great potential for overrating the role of temperature if that of aqueous fluids is incorrectly neglected.

Metamorphic petrology also has brought a new awareness of microchemistry and microtextures. Many minerals display internal chemical disequilibrium that can be assigned to a discrete mineral-forming episode (Vance *et al.*, 2003). It is tautological, yet sometimes forgotten, that the ubiquity of disequilibrium textures implies that diffusive reequilibration was negligible.

The third recent development in experimental petrology is the growing data-base of diffusivity determinations. As pointed out by Dahl (1997), from first principles it is expected that all phenomena that derive from the strength and length of interatomic bonds in a mineral structure (diffusivity, solubility, Mohs hardness, susceptibility to hydrothermal alteration, etc.) all follow the same ordered sequence both within a mineral family and between families. However, establishing a relative sequence is only a partial success, as a quantitative exploitation requires an absolute calibration. Natural diffusivities in anhydrous systems are quite low, as verified by virtually every recent investigation (e.g. «...rutile is more resistant to Pb loss through volume diffusion than previously thought»: Cherniak, 2000). Indeed, slow diffusion causes spectacularly sharp age variations in monazite and zircon (Cherniak and Watson, 2003). Sharp age gradients are now increasingly recognized in many more mineral chronometers (e.g. variations of ^{39}Ar-^{40}Ar ages in muscovite on a scale < 100 μm: Hames and Cheney, 1997; Di Vincenzo *et al.*, 2004). This presents a paradox: on one hand, growing evidence supports a very low volume diffusion rate for most minerals, substantially lower than was thought 20 years ago; on the other hand, these same minerals can be rejuvenated in nature. The solution to this paradox lies in the petrological observations of the ubiquity of aqueous fluids.

Pure volume diffusion in a «dry» system is exceedingly slow. It is observed comparatively

rarely in terrestrial systems, because wherever water is available, diffusion is overrun by recrystallization, which ensures a more rapid exchange of major and trace elements. «Wet» recrystallization can take place at any temperature within the stability field of the studied mineral, in particular at low temperatures, at which volume diffusion is negligible. Not taking into account the textural evidence for recrystallization (zoning, patchy textures, microchemical disequilibrium, etc.) has, in the past, misled geochronologists to infer that any isotope exchange is due to volume diffusion, which therefore was thought to be much faster than it really is. As recrystallization is mainly a function of the availability of aqueous fluids, and only subordinately of temperature, it follows that isotopic transport, which is controlled by recrystallization, should be more aptly considered a «geohygrometer» rather than a «geothermometer».

The extremely close interplay between mineralogy and isotope systematics is a consequence of the atomic forces that dictate the transport of isotopes in mineral structures. Thus one can combine two pieces of information: the P-T record provided by the main element composition, and the age and water activity information recorded by the radiogenic isotopes. Combining them clarifies the petrogenetic relationship between the individual components of the mineral mixture.

Bulk dating methods

In the past, a large body of analyses on metamorphic minerals were performed using bulk dating methods such as K-Ar and Rb-Sr. Because of the ubiquitous disequilibrium microtextures in most minerals, bulk data are very frequently incorrect and purely isotopic data without attending petrological and microchemical documentation are useless.

Moreover, K-Ar and Rb-Sr are applied to minerals having a high partition coefficient for alkali elements, usually micas and K-feldspar. Both can be problematic in their own right. High-alkali minerals have weaker average bonds. This makes them more prone to undergo isotopic exchange and/or alteration (Dahl, 1996; Parsons *et al.*, 1999). As a consequence, a very extensive characterization is required when analyzing alkali-rich minerals; when a microchemical study is missing, it is almost impossible to assess the reliability of a literature mica or feldspar age. Lack of stoichiometry is a certain sign of alteration and of questionable ages.

As for Rb-Sr data, it is vital to keep in mind that in a metamorphic rock the whole-rock system is rarely in equilibrium with all of its constituents; rigour requires to regress only minerals belonging to a specific paragenesis, avoiding relics and replacements. The whole-rock system is easily perturbed, as both Rb and Sr are extremely mobile elements. Fluid-induced mobility is well documented (e.g., Krogh and Davis, 1973), and their results make it clear that any Rb-Sr data that include whole-rock measurements must be treated with great suspicion.

Sm-Nd and Lu-Hf are increasingly being used to date garnet-bearing (HP and HT) metamorphism (Thöni and Jagoutz, 1992; Duchêne *et al.*, 1997), because garnet enriches parent elements Sm and Lu over daughters.

The assumption of initial isotopic equilibrium has been found to be the main stumbling-block by Thöni and Jagoutz (1992). In the eclogitic parageneses that they analyzed by Sm-Nd, they observed that divalent cations had achieved sufficient mobility to give rise to jadeite and garnet in mutual equilibrium, but trivalent rare earths had not equilibrated. It is important to repeat here that this insight was gained because overdetermined isochrons (with „ 3 minerals) failed to give acceptable dispersions, while at the same time inter-sample comparisons also showed no reproducibility.

The same cautions on initial isotopic disequilibrium apply in principle to the Lu-Hf dating of garnets as well. An additional difficulty peculiar to this latter method is the

possible presence of μm-sized inclusions of non-cogenetic zircon, which could be detrimental to an accurate age determination as they can dominate the garnet budget. The Hf atom can substitute the Zr atom in zircon, which therefore can contain up to 4% Hf. Only inclusions of a perfectly inheritance-free zircon population, which is strictly cogenetic with the garnet, do not bias a Lu-Hf age.

SPATIAL RESOLUTION AND SEQUENTIAL RELEASE

U-Pb analyses

In order to take into account mineralogical heterogeneities, some analytical protocols allow to extract the isotopic signature from a pre-defined subgrain.

U-Pb dating of spots within zircon by microbeam can be achieved by secondary ion mass spectrometry (Compston *et al.*, 1984) or by laser ablation plasma ionization multicollector mass spectrometry, LA-PIMMS (Parrish *et al.*, 1999; Foster *et al.*, 2002; Scherrer *et al.*, 2002). The petrogenesis of metamorphic zircon can be understood by a very thorough preliminary investigation by BSE or cathodoluminescence (CL) imaging (Gebauer *et al.*, 1988; Vavra *et al.*, 1996). Figure 1a is a sketch illustrating a metamorphic zircon. A young metamorphic rim (labelled R) overgrows an old detrital core (labelled C).

The U-Pb dating method yields three ratios providing age information: the $^{206}Pb^*/^{238}U$, $^{207}Pb^*/^{235}U$, and $^{207}Pb^*/^{206}Pb^*$ ratios (asterisks denote the «radiogenic» Pb, after subtraction of «common» Pb calculated from ^{204}Pb). The three independent age values are compared in order to assess whether the mineral behaved ideally. If it did, all three ages are equal to each

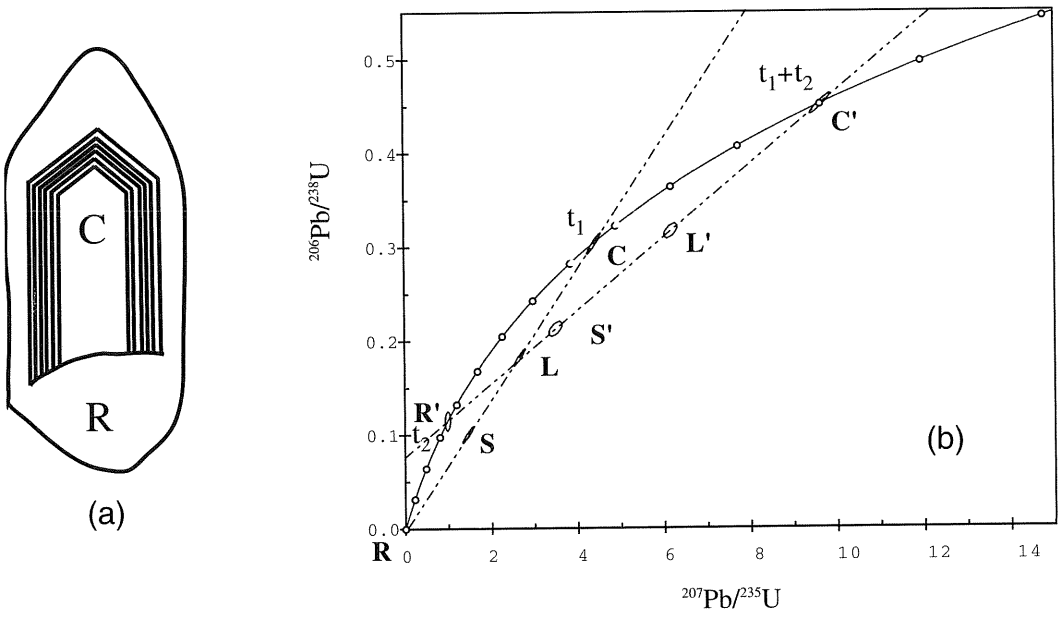

Fig. 1 – (a) Sketch of a metamorphic zircon. A broken detrital core, C, is overgrown by a metamorphic rim, R. Cathodoluminescence images very frequently identify magmatic oscillatory zoning in cores, while metamorphic rims are usually featureless. (b) Concordia diagram presentation of schematic U-Pb data on the zircon of Fig. 1a. At the time of metamorphism, t_1, point C (core) lies on the concordia curve; point R (rim) is Pb*-free and lies at the origin. Bulk analyses for large and small grains, L and S, plot on a discordia chord; the degree of discordance reflects the Pb mass balance of the core-rim mixture. Points R', S', L' and C' represent the evolution of the four points some time t_2 after metamorphism.

other («concordant»). If the ^{238}U-^{206}Pb age is different from the ^{235}U-^{207}Pb age, the two are called «discordant», and the Pb*/U ratios give geologically meaningless ages. The $^{207}Pb^*/^{206}Pb^*$ ratio may (but need not) preserve meaningful age information.

A graphical representation depicting concordance and discordance was devised by Wetherill (1956). In a plot of the $^{206}Pb^*/^{238}U$ against the $^{207}Pb^*/^{235}U$ ratio, for every abscissa value there is one and only one ordinate value corresponding to the same age. The locus of points having two concordant U-Pb ages is a curve called «concordia», shown in Fig. 1b. Its equation is $y = (x+1)\beta-1$, where $\beta = 0.15751$ is the ratio between the decay constants of ^{238}U and ^{235}U. The evolution of a U-bearing mineral can be visualized on this diagram. When the mineral is formed, it contains no radiogenic Pb*, and plots at the origin. As time passes, an undisturbed mineral in ideal conditions will accumulate Pb*; after some time t_1, its Pb*/U ratios have increased concordantly, and the mineral plots at point C on the concordia curve (Fig. 1b). A metamorphic disturbance results in the formation of clearly identified rims or patches. The newly formed rim is initially is free of Pb* and therefore plots at the origin (point R). The bulk mineral is a binary mixture of old, Pb*-rich and new, Pb*-free zones. Therefore, a large crystal with a high core/rim mass ratio is represented by point L lying on the segment CR; point S represents a small crystal with a higher relative proportion of rim material.

After some more time t_2, the core's radiogenic Pb increase due to ingrowth shifts point C towards higher $^{206}Pb^*/^{238}U$ and $^{207}Pb^*/^{235}U$ ratios, i.e. to point C' that still lies on the concordia curve. The rim, in turn, increases its radiogenic Pb* concordantly as well, to point R'. The points representing the aged bulk mineral, L' and S', lie on the C'R' tieline, being binary mixtures of R' and C'.

Spotwise analyses mostly give concordant C'-type and R'-type results, provided that a mineralogically uniform zone was chosen on the basis of CL or BSE images. However, before the availability of CL/BSE criteria to locate spatially resolved analyses, random microbeam analyses and especially multigrain bulk analyses had given thousands of «discordant» results. A lively debate on the nature of discordance has raged for decades. Initially, discordance was ascribed to diffusive loss of Pb due to a thermal disturbance (Tilton, 1960). This working hypothesis mirrored the limited awareness of the geochronological community for petrological processes; this was a time when even loss of Ar from sylvite was believed to reflect dry thermal events (Gentner *et al.*, 1954). The present understanding of the mechanisms controlling the spatial distribution of U-Pb ages, based on new diffusivity data (Cherniak and Watson, 2003), is that Pb is immobile in crystalline, non-metamict zircon. Microbeam analyses confirm that zircon and monazite never lose Pb by diffusion (Compston and Kröner, 1988; Vavra *et al.*, 1996; Cocherie *et al.*, 1998; Crowley and Ghent, 1999). Instead, data demonstrate the overwhelming role of recrystallization for Pb isotopic exchange: zircon cores accrete a rim whose chemical signature is a powerful petrological indicator of the various P-T-A-X conditions that prevailed when the different zircon generations were formed (Whitehouse *et al.*, 1999; Rubatto, 2002), and monazites develop patchy replacement zones under the influence of fluids (Cocherie *et al.*, 1998; Crowley and Ghent, 1999; Vavra and Schaltegger, 1999). The spatial resolution that can be achieved by microbeam analyses is around 20 μm diameter circular spots for ion microprobe and LA-PIMMS, and 2 μm for electron microprobe and micro-X-ray fluorescence analyses of REE phosphates.

In contrast to metamorphism, weathering can remove Pb from zircon (Krogh *et al.*, 1982). Old and/or U-rich minerals accumulated radiation damage, and thus are more susceptible to leaching by meteoric water even at ambient temperature. This particular «recent Pb loss» results in a usually moderate displacement of the bulk mineral point towards the origin.

The U-Pb method can also be applied with a stepwise leaching protocol (Frei *et al.*, 1997). Sequential release of Pb is achieved by successive leaching with different acids so as to discriminate common Pb from radiogenic Pb*. Furthermore, this technique makes it possible to recognize and correct for the presence of heterochemical inclusions, by partitioning Pb* into mineral matrix and inclusions (Schaller *et al.*, 1997). This provides help in dating metamorphic index minerals such as garnet (Kreissig *et al.*, 2001) and staurolite (Frei *et al.*, 1995).

Comparison of U-Pb and Rb-Sr results on the Sesia Zone eclogites (Oberhaensli *et al.*, 1985; Rubatto *et al.*, 1999) has shown an age discrepancy: the Rb-Sr age is ca. 120 Ma, higher than the U-Pb age of ca. 60 Ma. This could mean that eclogitization is Early Cretaceous, and U-Pb gives a «cooling age»; however, as zircon loses no Pb at eclogitic temperatures (Cherniak and Watson, 2003), it is the Rb-Sr age that is incorrect. By analogy with «excess Ar», one could propose that «excess Sr» was introduced from an external source. It must be kept in mind that «excess Ar» is often invoked to explain away uncomfortably high ages, but only rarely is there a rigorous distinction from inherited Ar. Inherited Ar and Sr are radiogenic daughters that were present in the precursor minerals and never were totally reequilibrated during the formation of the peak metamorphic paragenesis (cfr. Thoeni and Jagoutz, 1992). In the Sesia case, the survival of Permian relics in the Paleocene eclogitic minerals is the most likely explanation.

^{39}Ar-^{40}Ar analyses

The only other widely applied dating method which is routinely used to obtain isotope data that go beyond bulk analyses is the ^{39}Ar-^{40}Ar method. The closest analogy with U-Pb microbeam dating is the use of a laser beam to melt or vapourize selected spots of a mineral; this analytical technique will be treated at the end of this paragraph.

Far more widespread is the ^{39}Ar-^{40}Ar stepheating technique (Merrihue and Turner, 1966), which extracts the sample Ar in a series of heating steps instead of bulk degassing. This allows the calculation of an «internal» isochron from the Ar released in different steps of a single mineral, if the sample has never been perturbed since its formation. In perturbed whole rocks isochron diagrams fail to give an alignment: in a polymineralic system the metamorphosed phases are not cogenetic, and violate the prerequisites for isochron formation.

In the Berkeley approach (Merrihue, 1965), the neutron irradiation was designed to detect all elements from which Ar isotopes are produced in the nuclear reactor: K, Ca, and Cl. Indeed, an ^{39}Ar-^{40}Ar analysis yields the concentrations of these three elements and their ratios to radiogenic ^{40}Ar (Ar*) and to common isotope ^{36}Ar. From five concentrations it is always possible to construct four isotope ratios having a common denominator. To first order, Ar isotopic ratios (such as e.g. ^{37}Ar/^{38}Ar) mirror the chemical signature (in this example, the Ca/Cl ratio); second-order perturbations, such as those due to differential recoil of ^{39}Ar, ^{38}Ar and ^{37}Ar are negligible in samples whose relevant grain sizes are >> 1 μm. The four ratios constructed from the five Ar isotopes define the coordinate axes of a four-dimensional space. If e.g. the common denominator is K-derived ^{39}Ar, the four-dimensional space is formed by the ratios Ca/K, Cl/K, Ar*/K, and Ar_{tr}/K (tr denoting the trapped non-radiogenic ^{36}Ar and ^{40}Ar). Every three-isotope correlation diagram is a two-dimensional projection of a four-dimensional distribution of data points (Villa, 2001). It is easily demonstrated that binary mixtures are represented by straight line segments, and mixtures between N reservoirs by N-polygons. The main difficulty in determining the exact number of Ar reservoirs present in a sample is the projective distortion from four dimensions to two: a steeply inclined, non-planar N-polygon may project into what looks like a straight line (Belluso *et al.*, 2000, Fig. 9a). It is therefore necessary to investigate as many

correlation diagrams as possible so as to identify the minimum number of polygon corner-points.

Why should one be concerned about the Ca/Cl ratio in a mineral, if the age is calculated from the Ar/K ratio? The answer lies in the observational evidence that minerals are very seldom pure phases, as they rather consist of heterochemical mixtures (Villa *et al.*, 1997, 2000; Di Vincenzo and Palmeri, 2001). Monitoring all chemical indicators for each heating step allows to recognize whether a monogenetic mineral is being analysed or a mixture, and if so, which steps pertain to the different reservoirs. The coexistence of more than one generation of the same mineral family, each with a different age, is strong evidence that accretion/replacement occurs without resetting the isotopic record of the petrographically relict reservoir.

A very popular visualization of ^{39}Ar-^{40}Ar data is the age spectrum diagram (Fig. 2a), in which the age of individual heating steps is plotted against the cumulative release of an Ar isotope, most frequently ^{39}Ar. The interpretive difficulties can be numerous for some samples

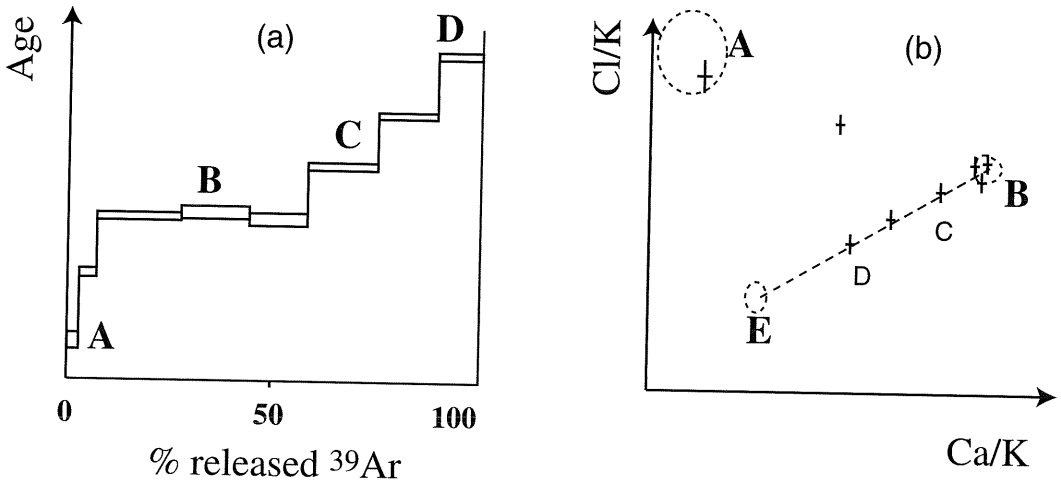

Fig. 2 – (a) Age spectrum diagram. The abscissa is the cumulative release of ^{39}Ar, the ordinate is the calculated step age. The height of the boxes is the age uncertainty. In this example (an amphibole from a metamorphic rock) four portions of the spectrum can be described: in the first heating step(s), denoted by A, the apparent age is low; ages become constant at higher degassing temperatures (B), then rise in the last heating steps (C, D). Only a small part of the relevant information on the sample is provided by the age spectrum *per se*, and additional clues on the mineralogical identity of the Ar reservoirs must be derived by other means, such as comparing microchemical analyses with Ar isotope correlation diagrams (see Fig. 2b).
(b) Ar isotope correlation diagram. The abscissa and the ordinate are constructed from the ^{37}Ar, ^{38}Ar and ^{39}Ar measured in each heating step. Three regions can be identified on the basis of electron probe microanalyses (dashed fields): A, low-Ca, high-Cl secondary phases (phyllosilicates, clays); B, chemical composition of amphibole generation Am_2; E, chemical composition of amphibole generation Am_1. The stepheating results are plotted as crosses and can be directly compared to the sample mineralogy. The distribution of data-points inside triangle ABE mirrors the presence of three Ar reservoirs. The first heating step with its high Cl/K ratio and low age must be viewed as degassing of secondary alteration phases. The subsequent heating steps with constant Ca/K, Cl/K and Ar/K ratios are identified as Ar released only by amphibole generation Am_2; the closer the chemical match, the more accurate the age assignment. The steps with increasing ages (C, D) do not match the chemical composition of any single mineral; because of the regular trends of the Ca/K, Cl/K and Ar/K ratios they must be viewed as binary mixtures between reservoirs B and E. The chemical signature of amphibole generation Am_1 as determined by electron microprobe is never found in the heating steps: this means that Am_1 never is the only reservoir releasing Ar, and that its Ar is always accompanied by some Ar released by Am_2. The age of generation Am_2 is given by the steps having the chemical signature of field B; that of Am_1 is found by extrapolating the age trend defined by steps B, C, D to the known chemical composition E.

if one only considers age spectra, without taking into account the additional information provided by all 5 Ar isotopes. Fig. 2b shows one such chemical diagnostic diagram, illustrating three reservoirs present in an amphibole separate: minor Cl-rich alteration phases, and two amphibole generations, Am_1 and Am_2; although they have different ages, they can be reliably dated (Villa *et al.*, 2000).

On the basis of the Cl/K ratios of white micas, Tomaschek *et al.* (2003) distinguished high-pressure paragonites from much younger greenschist-facies muscovite replacements. By additionally taking into account zircon morphology and ages, as well as fluid inclusions, they were able to reconstruct the effects of a high-pressure aqueous fluid phase on the development of the eclogitic paragenesis.

Insight on mineral mixtures gained from metamorphic minerals (amphiboles, feldspars, micas) equally well applies to all other polymineralic systems (basalts, shales, etc.). As an example, Müller *et al.* (2002) recognized the ages of Alpine faults by discriminating true pseudotachylyte matrix from younger alteration phases and from xenolithic clasts on the basis of its chemical signature.

Partial outgassing can also be achieved by laser-induced melting and/or vaporization of selected small spots so as to obtain spatially resolved ages (Megrue, 1973). All five Ar isotopes are released from that spot only; this allows to obtain a spatial map of the age distribution and of the distribution of Ca, Cl and K. Isochrons can also be obtained by regressing together laser spot analyses, provided they all were obtained on a monogenetic and isochemical mineral generation.

The spatial resolution of ^{39}Ar-^{40}Ar laser microanalyses is not limited by the size of the beam (which can be focussed to below 1 μm) but by the counting statistics of available Ar atoms. With present-day mass spectrometer sensitivities a meaningful analysis of a Phanerozoic sample requires 10^4-10^5 μm^3 (Müller *et al.*, 2002) and even then the minor Ar isotopes 36, 37 and 38 are sometimes at or below the detection limit. Analyses that do not report the latter three isotopes are of very limited practical value, because the microchemical information was shown to be decisive for a correct interpretation of the role of heterochemical recrystallization.

Charting the actual spatial distribution of Ar isotopes constrains the physical basis of Ar transport. Onstott *et al.* (1990) investigated if volume diffusion occurs at all in terrestrial systems, and to what extent volume diffusion can be detected when superimposed on faster processes such as fluid-induced recrystallization.

The reproducible observation that micas having a zoned Ar concentration give step-heating «plateau» (Hodges *et al.*, 1994; Foland, 1983) implies that volume diffusion does not occur in laboratory degassing of hydrous minerals (Sletten and Onstott, 1998). This in turn implies that an age spectrum does not, as a rule, mirror the spatial distribution of Ar in hydrous minerals.

The use of laser spot dating («age mapping») has been successfully applied by Di Vincenzo *et al.* (2001, 2003, 2004) both to unravel the metamorphic history of rocks from Antarctica and Sardinia and to understand the systematics of Ar retention as a function of recrystallization, and not of diffusion.

CONCLUSIONS

Dating metamorphic events requires that the metamorphic disturbance was sufficiently vigorous to achieve isotopic equilibration among some minerals of a rock, and that none of these minerals subsequently underwent chemical re-equilibration during the rock's retrogressive path during exhumation to the surface.

Magmatic events very often achieve complete isotopic equilibration among a rock's minerals; dry metamorphism usually doesn't. Because water-present diffusivity is orders of magnitude faster than the water-absent one, the

temperature history of a rock is of secondary importance for its isotopic record compared to the history of its water activity. As a result, isotopic geochronology applied to metamorphic rocks is capable of dating fluid circulation events. It is essential to realize that fluid circulation events can occur over a large temperature range and are therefore inherently poor thermometers.

What isotopic geochronology of metamorphic minerals can offer instead are insights into P-T-A-X histories; if isotopic analyses can be coupled to microchemical and microstructural investigations on the metamorphic minerals, the history of deformation can be added, and the whole metamorphic evolution of a rock can be reconstructed.

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